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HYDROGEN ION CONCENTRATION AND ITS APPLICATION TO WATER PURIFICATION¹

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It is quite probable that most of those present are wondering just what hydrogen ion concentration is and why, whatever it is, it should appear on this program. It probably suggests some of the mysteries with which chemists from the time of alchemists to date have been popularly supposed to occupy themselves.

The purpose of this paper is to attempt to tell what the hydrogen ion concentration is and why it is of interest to waterworks men. Most of them have some idea what is meant when one speaks of an alkaline solution and an acid solution. All know that the things called acids usually have a sour taste, and what are called alkalis have a soapy taste. All know, also, that there are certain colored compounds, such as litmus and methyl orange, which have one color in an acid solution and another in an alkaline solution. As will later be shown, different indicators do not give the same result in many acids. Some of those present may have heard the excellent paper on this subject given by Dr. Washburn before this society in 1910.

Hydrochloric acid, or as it is commercially called, muriatic acid, is made up of hydrogen and chlorine, HCl ; nitric acid is HNO_3 , sulphuric acid, H_2SO_4 ; acetic acid, HAc , the Ac being a short abbreviation for a complex radical made up of carbon, hydrogen and oxygen; and boric acid, H_2BO_2 often called boracic acid. The only thing common to them all is hydrogen, and it is natural to conclude, therefore, that the properties persons normally think of in an acid must be due to the hydrogen. Now consider the chemical formulas for certain of the better known alkalies, NaOH , KOH , Ca(OH)_2 , etc. The common constituent is the OH radical made up of oxygen and hydrogen, and it is to this radical that the characteristic basic properties must be attributed. The OH and H , if taken together, make up the elements of water.

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While all acids have certain properties in common they do not always have these properties to the same degree or intensity. Take solutions of three acids, equal volumes of each solution containing equivalent amounts of acid. The first is hydrochloric or muriatic acid; most of those present know that this acid, even in quite dilute solutions, say 3 per cent, has an extremely sour taste, in fact it will quite severely burn the tongue and even the tougher skin of the hand. The second acid solution is acetic, the acid found in vinegar; ordinary vinegar is about 3 to 4 per cent acetic acid and everyone knows that it is only pleasantly sour, hardly burning the tongue at all. If one were so rash as to place some in his eye he would suffer some inconvenience. Those here may never have tried this, but some may have had sour orange juice spattered in his eyes and that is about the same as vinegar. The third solution is boric or boracic acid. This, in from a 3 to 4 per cent solution, is a popular eye wash, causing no discomfort when dropped in the eye and does not have a sour taste at all. These three solutions, in addition to affecting the senses differently, also do not affect all indicators in the same manner. Just as the sense of taste and feeling vary with the intensity of the acid reaction, indicators are also of different sensitivity. For instance, thymol blue, which is red in acid solutions and yellow in alkaline solutions, is not very sensitive, being only affected in the strongest acids. If a small portion of the indicator is added to each of the three acid solutions already mentioned, the hydrochloric acid turns the indicator red but that the other two make it yellow. To this indicator, therefore, the acetic and boric acids are alkaline. Another indicator, bromphenol blue, is yellow in acid solution and blue in alkaline. It is somewhat more sensitive to acids. Adding it to the three acid solutions, the hydrochloric and acetic acids react acid, but the boric does not. A third indicator, bromthymol blue, which is very sensitive to all acids, is also yellow in acid solutions and blue in alkaline. Adding it to the three acid solutions, each gives an acid reaction to this indicator. A little of this third indicator added to a solution of sodium hydroxide, which is strongly alkaline, will turn it blue. This is sufficient to show that while one may take equivalent amounts of different acids there is a certain difference in the intensity of the acid properties.

It has been found by a large number of experiments that any acid, when put into solution in water, tends to break apart into the hydrogen ion and other ions of which it is composed. In the case

of hydrochloric acid, hydrogen ions and chloride ions would be produced. Acetic acid gives hydrogen ions and acetate ions, the latter being rather complex radicals which chemists abbreviate into Ac. Boric acid gives hydrogen ions and borate ions. This splitting up into ions is called "ionization." Now it has also been proved that not all acids ionize to the same extent. For example, in the hydrochloric acid solution the hydrochloric acid ionizes about 90 per cent, but the acetic acid only ionizes about 2 per cent, and the boric acid ionizes only very slightly indeed, about 0.005 per cent. An acid which ionizes greatly is called a strong acid, and it will have the very sour taste, ability to smart and burn the skin and give an acid color to all indicators, like hydrochloric acid. Those that do not ionize to such a great extent are called weak acids and the above mentioned properties vary in intensity according to the amount of ionization.

From this reasoning, it will be seen, therefore, that the sour taste and ability to change indicators depend not upon the total amount of acid per unit volume but upon the total amount of ionized hydrogen per unit volume. And that is what the hydrogen ion concentration is, the total amount of ionized hydrogen per unit volume of the solution under consideration. Alkalies ionize in a similar manner, as do all salts. The properties of the alkalies depend upon the extent of the ionization in a way similar to the acids.

In most natural water carbon dioxide or carbonic acid is present in solution. This is a very weak acid like the boric acid, but it is an acid and gives a definite hydrogen ion concentration. This hydrogen ion concentration has recently attracted much attention. Biologists have found that the small plants and animals growing in water are much affected by changes in it. Some organisms are unable to exist in certain streams because of too high or too low hydrogen ion concentration. For this reason considerable interest is attached to the determination of the hydrogen ion concentration of surface waters. One way of making this determination is by means of indicators. An indicator is selected which changes color at about the hydrogen ion concentration that the water is thought to be. A small portion is placed in a solution of known hydrogen ion concentration, an equal amount is placed in a sample of the water being examined and the colors are compared. If the color is the same, the hydrogen ion concentration of the water is the same as that of the known solution; if the colors are different, known solutions with different hydrogen ion concentration are tried until a match is obtained. Making compari-

sons in this way and having at hand a selection of indicators and a set of solutions of known compositions the hydrogen ion concentrations of which vary in a progressive manner, it is practicable to make these determinations quite accurately. There are other and, for some purposes, better methods of making these determinations but there will not be time to go into them here.

The hydrogen ion concentration also has a great deal to do with whether or not water will corrode metals. It is possible to illustrate this in a rather gross manner with the same acids which were previously selected as types. If a piece of zinc is dropped into the hydrochloric acid, which has a high hydrogen ion concentration, a good deal of gas rises, indicating that the metal is dissolving or corroding rapidly. If zinc is dropped in the acetic acid, which has a lower hydrogen ion concentration, there is also an evolution of gas but not nearly so much. The boric acid solution, which has a very low hydrogen ion concentration, has no apparent effect on the zinc. It has long been known that free carbon dioxide or carbonic acid in water would cause the water to be corrosive; the experiments just mentioned show that the corrosive effect is to a considerable extent due to the hydrogen ion concentration built up by the carbonic acid. Two waters containing the same amount of free carbonic acid do not necessarily have the same hydrogen ion concentration and do not, therefore, have the same corrosive action. The hydrogen ion concentration produced by an acid varies inversely with the concentration of the other ion with which the hydrogen is associated in the acid. A water that contains 10 parts per million of carbonic acid will have a much higher hydrogen ion concentration and be, therefore, more corrosive than one containing the same amount of carbonic acid and say 200 parts per million of carbonates, for the carbonates, such as calcium and magnesium carbonates, also ionize to give carbonate ions and calcium or magnesium ions. This increase of carbonate ions serves to decrease the hydrogen ion concentration. This effect, which is called the common ion effect, can be illustrated by means of acetic acid. Into a tube containing acetic acid and an indicator which the acetic acid caused to show its acid color, add a small amount of sodium acetate, a salt of acetic acid and there results a great increase in the concentration of the acetate ions. There is also an almost immediate change of color of the indicator, showing that there has been a decided decrease in the hydrogen ion concentration. Therefore a study of the hydrogen ion concentration of natural waters

may serve to throw some light upon the probable effect of the waters upon metals. The same information cannot be obtained by simply determining the total amount of carbonic acid which the waters contain.

The third point of interest is the precipitation of the alum in the coagulation of water preliminary to sedimentation and filtration. The hydrogen ion concentration is of importance, since if the water is too acid or, as more commonly stated, deficient in alkalinity, the alum will be precipitated incompletely or not at all, making the use of lime necessary. Since this precipitation of aluminum depends upon the hydrogen ion concentration of the water, the proper control of the hydrogen ion concentration would be all that is necessary to obtain satisfactory coagulation results. It does not seem too much to hope that very soon automatic machines will be developed which will be controlled by the hydrogen ion concentration of the treated water and which will regulate the dosage of alum and lime that is to be added to the water.

The precipitation of calcium and magnesium in a water softening reaction is very similar to the alum coagulation and it would seem that in this case, the controlling of the softening plants by means of the hydrogen ion concentration might not be too much of a chemist's dream.

The State Water Survey Division is at present engaged in studying the last three reactions with a view to determining the changes in hydrogen ion concentration which take place throughout the progress of the reactions, with the hope that accurate information on this point will be of value in working out better methods of control.

Summary. To summarize, the hydrogen ion concentration of a water or for that matter of any solution is a measure of the extent to which the various acids and acidic compounds in the water are ionized or broken up into hydrogen ions and acid radicals. It is what might be termed the intensity factor of acidity as opposed to the quantity factor which is obtained by measuring the total acid or alkali found in the solution. The hydrogen ion concentration of water is of interest to water-works men, first because it is one of the factors controlling the life of animal and vegetable organisms in the water; second, because it is one of the factors in corrosion; and, third, because the study of this hydrogen ion concentration offers a possible improved means of controlling the coagulation and water-softening reactions used in water purifications.